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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

This invention relates to the method of forming coating on a substrate especially using atmospheric pressure plasma discharge, the method of polymerizing polymer formation material, and the device for forming coating on a substrate further about the method of forming coating on a substrate.

[0002]

For example, since surface activity is increased in order to protect a substrate from corrosion, to provide the barrier to oxidation and to improve an adhesive property with other materials, a substrate can be coated for various Reasons for the biomedical conformity of a substrate. The method generally used in order to embellish or coat a substrate face is placing a substrate into a reaction vessel and performing plasma discharge. Many examples of such processing are known for the art concerned, for example, US,5,876,753,B indicates the process for making target material adhere to a solid surface, and this process, It includes adding a carbon system compound to the surface by low-power output variable duty cycle pulse plasma vacuum evaporation. The Europe public presentation No. 0896035 indicates the device which has a substrate and coating, and coating is performed to a substrate by the plasma polymerization of the gas containing at least one organic compound or a monomer. Germany patent No. 19924108 which began and was exhibited after the priority date of the beginning of this application indicates the process for coating a color and corrosion inhibitor on a substrate. Performing liquid thin film coating, and performing plasma polymer protective coating continuously on a substrate, is included by the process. Plasma polymer coating is formed using a gas monomer and low pressure plasma.

[0003]

However, in such a plasma surface treatment, to place a substrate under a decompression condition is needed, therefore a vacuum chamber is needed. The usual coating formation gas pressure is the range of 5 Nm^{-2} - 25 Nm^{-2} (1 atmosphere = see the $1.01 \times 10^5 \text{ Nm}^{-2}$). As a result which needs decompression, the surface treatment is expensive and it is limited to batch processing, and the coating formation material must be a gestalt of a gas or a steam, in order to hold decompression conditions.

[0004]

This invention persons discovered that the above-mentioned disadvantageous state of substrate face plasma treatment was conquerable using the combination of atmospheric pressure plasma

discharge, and a spray liquid object and/or a solid coating formation material.

[0005]

Therefore, according to this invention, it is provided by the method of forming coating on a substrate, and a described method, It includes introducing the coating formation material of a spray liquid object and/or a solid into the ionizable gas style generated from atmospheric pressure plasma discharge and/or it, and exposing the above-mentioned substrate to a spraying coating formation material.

[0006]

It should be understood that the coating formation material by this invention is the material which can be used in order to produce arbitrary suitable coating containing the material which can be used, for example in order to grow up a thin film, or since the existing surface is embellished chemically.

[0007]

This invention also provides the method of polymerizing polymer formation material, and a described method includes spraying polymer formation material and exposing the above-mentioned polymer formation material to atmospheric pressure plasma discharge.

[0008]

Provide this invention further and the device for forming coating on a substrate the above-mentioned device, A means for generating atmospheric pressure plasma discharge by which the above-mentioned substrate is arranged at the inside at the time of use, the spray pump for providing a spraying coating formation material in plasma discharge, and the means for supplying a coating formation material to the above-mentioned spray pump are included.

[0009]

Every conventional means for generating atmospheric pressure plasma glow discharge can be used in this invention, for example, an atmospheric pressure plasma jet, atmospheric pressure microwave glow discharge, atmospheric pressure glow discharge, etc. are mentioned. Usually, in order for such a means to generate uniform glow discharge in atmospheric pressure according to a Penning ionization mechanism, . A helium diluent and a high-frequency (for example, >1kHz) power supply can be used. (For example) Kanazawa and others and J. Phys.D: . Appl. Phys. 1988 and 21, 838, Okazaki and others, and Proc.Jpn. Symp. Plasma Chem. 1989, 2, 95, Kanazawa and others, and Nuclear. Instruments and Methods in Physical Research 1989, B37/38, 842 and Yokoyama and others, J. Phys. D: Refer to Appl. Phys. 1990, 23, and 374.

[0010]

A coating formation material may be sprayed using which conventional means, such as an ultrasonic nozzle, for example. It is desirable still more preferred to generate a coating formation material drop with a size of 10-100 micrometers, and a spray pump is 10-50 micrometers. A suitable spray pump to use it by this invention is an ultrasonic nozzle from Sono-Tek Corporation, Milton, New York, and USA. The case where the device of this invention is used for a device forming copolymer coating on a substrate from two different coating formation materials, for example, or [that a monomer is nonmiscible] -- or it exists in a different phase, for example, the 1st phase can contain two or more especially helpful spray pumps, when the 2nd phase is a gas or a fluid in solid form.

[0011]

This invention can be used in order to form substrate coating of the type with which many differ. The type of coating formed on a substrate is determined by the coating formation material (singular number or plurality) used, and the method of this invention may be used in order to

polymerize a coating formation monomer material (singular number or plurality) on a substrate face (copolymerization). Coating formation materials may be organic or inorganic solids, fluids or gases, or those mixtures. As a suitable organic coating formation material, carboxylate, methacrylic acid ester, Acrylic ester, styrene, a methacrylonitrile, an alkene, and diene, For example, methyl methacrylate, ethyl methacrylate, methacrylic acid propyl, Butyl methacrylate, other alkyl methacrylate, and corresponding acrylic ester, organic functional methacrylic acid ester and acrylic ester are included (glycidyl methacrylate.) Methacrylic acid trimethoxysilylpropyl, methacrylic acid allyl, methacrylic acid hydroxyethyl, Methacrylic acid hydroxypropyl, methacrylic acid dialkylamino alkyl, And the methacrylic acid containing meta-(acrylic) acid fluoro alkyl, Acrylic acid, fumaric acid and ester, itaconic acid (and ester), A maleic anhydride, styrene, alpha-methylstyrene, a halogenation alkene, For example, vinylic halide, such as VCM/PVC, vinyl, fluoridation, and a fluorination alkene, for example, a perfluoro-alkene, acrylonitrile, a methacrylonitrile, ethylene, propylene, allylamine, halogenation vinylidene, butadiene, Acrylamide, such as N-isopropylacrylamide, methacrylamide, An epoxy compound, for example, glycidoxy propyltrimethoxysilane, Glycidol, styrene oxide, butadiene monooxide, ethylene glycol, Diglycidyl ether, glycidyl methacrylate, bisphenol A diglycidyl ether (and the oligomer), The Lynn content compounds, such as for example, conductive polymer, such as vinyl cyclohexane oxide, pyrrole, thiophenes, and those derivatives, and dimethylallyl phosphonate, are mentioned. As a suitable inorganic coating formation material, the metal and the metallic oxide containing the colloidal metal are mentioned. An organic metallic compound is also a suitable coating formation material, and metal alkoxides, such as an alkoxide of a titanate, a tin alkoxide, zirconate, germanium, and erbium, are contained. However, when this invention persons provided a substrate with coating of a silica base or a siloxane base using the coating formation constituent containing silicon content material, they discovered that especially this invention was helpful. As a suitable silicon content material to use it by the method of this invention, Silang (for example, Silang, an alkyl halo silane, alkoxysilane). And a straight chain (for example, polydimethyl siloxane) and cyclosiloxane. (For example, octamethylcyclotetrasiloxane) (Cyclosiloxane.) [an organic functional straight chain and] (for example, the straight chain of Si-H content, halo functionality, and halo alkyl functionality, cyclosiloxane, for example, tetramethyl cyclotetrasiloxane, and Tori (monofluorobutyl) trimethyl cyclotrisiloxane) -- containing -- it is mentioned. For example, in order to fit the physical property of substrate coating to specific necessity, the mixture of a different silicon content material may be used (for example, optical properties, such as a heat characteristic and a refractive index, and viscoelastic property).

[0012]

Under oxidation conditions, the method of this invention can be used and oxygen content coating can be formed on a substrate. For example, coating of a silica base can be formed in a substrate face from a spraying silicon content coating formation material. Under a reducing condition, coating which does not contain oxygen using this invention can be formed, for example, coating of a silicon carbide base can be formed from a spraying silicon content coating formation material.

[0013]

For example, the plasma generation conditions containing gases other than oxygen, such as rare gas, air, hydrogen, nitrogen, and ammonia, can also be used. Nitrogen can combine with a substrate face in nitrogen content atmosphere, and a nitrate can join together and/or form on a substrate face in nitrogen and an oxygen containing atmosphere. Such a gas can be used, also in

order to pretreat a substrate face before exposing to a coating morphogenetic substance. For example, the oxygen content plasma treatment of a substrate can provide improvement of adhesion with performed coating. Oxygen content plasma is generated by introducing oxygen content material to the plasma of oxygen gas or water. Post-processing of the coating formed on the substrate may be carried out by various plasma conditions. For example, coating of siloxane origin may oxidize by oxygen content plasma treatment further. Oxygen content plasma is generated by introducing oxygen content material to the plasma of oxygen gas or water.

[0014]

Since the method of this invention is performed under atmospheric pressure conditions, the advantage of this invention exceeding conventional technology is being able to use the spraying coating formation material of both a fluid and a solid, and being able to form substrate coating. A coating formation material can be introduced under the nonexistence of carrier gas into the flow generated as plasma discharge or a result, i.e., a direct inlet can be directly carried out by pouring, for example, and a coating formation material is directly poured in by it into plasma.

[0015]

As mentioned above, this invention persons discovered that especially this invention was helpful, in order to form coating of a silica base and a siloxane base on a substrate using silicon content material. For example, although coating of a silica base can be formed in a substrate face from spraying silicon content material under oxidation conditions, such as an oxygen containing atmosphere, Under the conditions of not oxidizing, siloxane polymer, such as a straight chain, branching, or resin-like siloxane polymer, can be formed in a substrate face from spraying of a silicon content monomer. A siloxane organicity copolymer can be formed in a substrate face by use of the mixture of organicity and a silicon content monomer. Coating of a silica base may be formed in a substrate face, and then this may be coated, for example with the further materials, such as organicity or siloxane polymer. For example, when a siloxane is mixed with organic polymer and a substrate is formed from this mixture, a siloxane can be moved to the organic polymer body surface of a substrate for a difference of the surface energy between organic polymer and a siloxane. Next, if atmospheric pressure plasma treatment is performed to this substrate, the siloxane of a substrate face will oxidize and will form coating of a silica base. Processing which follows this invention by performing atmospheric pressure plasma treatment further under existence of a spraying silicon content monomer is carried out to coating of this silica base next, and siloxane coating is formed on it. However, this invention is useful also in order to, form organic coating of polyacrylic acid or perfluoro-organicity coating on a substrate for example.

[0016]

The substrate coated can include arbitrary materials, such as metal, ceramics, a plastic, a siloxane, ** or non-woven textile, a natural fiber, a synthetic fiber, a cellulosic material, and powder, for example. However, the size of a substrate is restricted by the size of the capacity to which atmospheric pressure plasma discharge is generated, i.e., an inter-electrode distance of a plasma generation means. In a typical plasma generator, plasma is generated in a mm [5 mm to / 50], for example, to 12, 25-mm gap. Therefore, this invention is especially helpful in order to coat a thin film, textiles, and powder.

[0017]

The substrate coated by the method of this invention can have various uses. For example, the coating of the silica base generated in an oxidizing atmosphere can strengthen the barrier and/or diffusing characteristic of a substrate, and can heighten the capability which the further material

pastes up on a substrate face. Halo functional organicity or the siloxane coating (for example, perfluoro-alkene) can increase the hydrophobicity of a substrate, sparse oiliness, fuel and soil tolerance, and/or a stripping characteristic. The polydimethyl siloxane coating can strengthen the water resisting property of a substrate, and a stripping characteristic, and can raise the softness of a feel of textiles. Polyacrylic acid polymer coating can be used as a part of laminated structure as a glue line for promoting adhesion to a substrate face. If coating is made to contain a colloidal-metal kind, surface conduction nature will be provided to a substrate, or the optical property will be improved. A polythiophene and polypyrrole give conductive polymer coating which can also provide corrosion resistance to a metal substrate.

[0018]

One main problem which is easy to generate when coating a substrate using the process of including plasma treatment is that the chemicals characteristic of the material used for formation of coating may lose. Therefore, the main advantages of this invention are that the chemicals characteristic of a coating formation material is substantially held in formed coating. For example, when acrylic acid is used as a coating formation material, the functionality of carboxylic acid is substantially held in formed coating.

[0019]

This invention provides the method of manufacturing the substrate which has a multilayer coating tip by the above-mentioned process. In this case, a coating layer is given, whenever it repeats atmospheric pressure plasma glow discharge to a substrate and passes it. By being conveyed through atmospheric pressure plasma glow discharge as an open reel type process, in such a case, can coat a substrate continuously preferably, and here, In order that the whole substrate may guarantee having predetermined holding time within glow discharge, a substrate passes glow discharge from the 1st reel at a fixed speed, and moves to up to the 2nd reel. each substrate -- glow discharge -- 1 time -- or -- multiple-times passage can be carried out -- thereby - the 1st of the 1st passage -- that is, a feed reel turns into a substrate recovery reel in the 2nd passage, the substrate recovery reel of the 1st passage is a feed reel in the 2nd passage next, and two reels are exchanged at the end of each passage. Or a series of atmospheric pressure glow discharge chambers may be passed by the substrate.

[0020]

For the desirable use of coating of the substrate coated according to this invention. The use as a component of in the organic light emitting diode device in oxygen for the adhesives of a layered product, for example, a foodstuffs packaging use, and/or the barrier of moisture, a flat-panel display, etc. or a top is included.

[0021]

This invention is explained here in detail with reference to an accompanying drawing.

[0022]

The device according to this invention shown in drawing 1 is provided with the means (roughly shown by 10) and spray pump (roughly shown by 12) for generating atmospheric pressure plasma discharge, and the spray pump 12 is connected to the syringe pump 14 for supplying a coating formation material to the spray pump 12. The ac power supply 20 with a high tension of 15 kHz supplied over the two aluminum electrodes 22 and 24 estranged 12 mm is included in the means 10 for generating discharge, and the lower live electrode (live electrode) 22 is intercepted with the glass dielectric plate 26. The spray pump 12 has the Sono-tek*8700-120 ultrasonic nozzle 30, and is connected to the Sono-tek*06-05108 broadband-ultrasound generator 32. The spray pump 12 is fixed in the ground electrode 24 on O ring 34. The substrate 40 coated is

arranged on the electrode 22 and the glass dielectric plate 26 between 24.

[0023]

The device explained in the preceding sentence with reference to drawing 1 was used for all the following procedures.

(*Sono-tek Corporation, Milton, New York 12547, USA)

[0024]

Working example 1

The polyethylene film board of the piece was cleaned ultrasonically in isopropyl alcohol and the 1:1 mixtures of cyclohexane, and it has arranged on a glass plate. After exhausting residual gas, plasma discharge gas was introduced by rate-of-flow 1900sccm and pressure $1.02 \times 10^{-5} \text{Nm}^{-2}$.

Two sorts of discharge gas, helium, and 99% helium / 1% oxygen mixture, was used. After purging for 10 minutes, the syringe pump 14 was switched on and the coating formation material was made to flow at the rate of $3 \times 10^{-5} \text{mls}^{-1}$. Two sorts of coating formation materials, octamethylcyclotetrasiloxane ("D₄" is called hereafter) and tetramethyl cyclotetrasiloxane ("D₄H" is called hereafter), were used. When the coating formation material reached to the ultrasonic nozzle, atmospheric pressure plasma discharge was caused by switching on an ultrasonic generator, in order to start spraying of a coating formation material (2.5W), and impressing 1.5 kV to an electrode. After continuing vacuum evaporation of a coating formation material for 10 minutes, the substrate was taken out, under decompression, it has arranged for 20 minutes and unstable material was removed.

[0025]

The result of the above-mentioned procedure is shown in the following table 1. Ultimate analysis of the substrate face was performed using x linear-light electronic spectroscopic analysis (Kratos ES300), and thickness was determined using the spectrophotometer (nkd-6000 of Aquila Instruments). The drop of 2micro of fixability 1 of deionized water was used, and angle-of-contact measurement was performed using the video capture device (VCA2500XE of AST Products).

[0026]

Gas transmittance measurement of the substrate face was also performed using the mass spectrometer. A result is shown in Table 2. The improvement factor of a barrier is calculated as [gas penetration of coated substrate]/[a gas penetration of a reference sample].

[0027]

[Table 1]

サンプル	XPS分析				接触角 (°)	蒸着速度 (nm s ⁻¹)	コーティング厚 (nm)
	%C	%O	%Si	%SiO _x			
理論	50	25	25	0	-	-	-
100%	43.3	29.3	25.8		107.8*	28	279
1%	25.5	48.5	26.0	74.4	56.4	29	286
H理論	33.3	33.3	33.3	0	-	-	-
H 100%He	32.5	39.1	28.4		102.3	82	
H 1%	9.2	61.4	29.5	81.5	ウェット	244	

浄なポリエチレンは接触角が105.8°である。

[0028]

[Table 2]

表 2	
サンプル	バリヤ改良因子
清浄ポリエチレン	1. 0 (定義による)
D ₄ , 100% He	0. 9
D ₄ , 1% O ₂	6. 8
D ₄ H, 100% He	0. 9
D ₄ H, . 1% O ₂	4. 5

[0029]

ATR-FTIR research of the substrate face showed that the ring opening polymerization of the D₄ and D₄H coating formation material occurred, and the polysiloxane was formed in the substrate face. In particular, it was shown by the ATR-FTIR research on the latter that polysiloxane coating holds many of Si-H functionality of D₄H.

[0030]

By NMR research of coating prepared to the glass surface as mentioned above. The polysiloxane formed in the substrate face by the polymerization of the D₄ and D₄H coating formation material, $2\text{SiO}(\text{CH}_3)_{2/2}$ unit of bivalence, and CH_3SiO_3 [tervalent] / 2 unit are included, namely, it was shown that a polysiloxane is resin-like.

[0031]

Working example 2

Acrylic acid was used as a glass substrate and a coating formation material, only helium was used as discharge gas, and the method of above-mentioned working example 1 was repeated. Coating was removed from the substrate before analysis.

[0032]

In FTIR of coating, and solid NMR analysis, it was checked that acrylic acid polymerized and polyacrylic acid had been formed. Each of FTIR(s) and NMR data showed consumption of unsaturation C=C combination.

[0033]

Working example 3

The method of working example 2 was repeated using nylon and a polyethylene board.

[0034]

It was checked that the acrylic acid coating formation material polymerized and polyacrylic acid coating had been formed in the substrate face by comparison of FTIR analysis of coating with commercial polyacrylic acid.

[0035]

x linear-light electronic spectroscopic analysis, thickness analysis, and angle-of-contact measurement were carried out according to above-mentioned working example 1. A result is shown in the following table 3.

[0036]

[Table 3]

表 3					
	X P S 分析			接触角 (°)	蒸着速度 (nm s^{-1})
	%C	%O	%CO ₂ H		
理論	60.0	40.0	33.3	—	—
市販のポリ アクリル酸	63.3	36.7	29.9	ウェット	—
実施例 3 の コーティング	62.6	37.4	26.4	ウェット	231±95

[0037]

It opted for the gas transportation which passes along the coated polyethylene film by mass analysis. The barrier improvement factor calculated by above-mentioned working example 1 was larger than an unsettled polyethylene board and commercial polyacrylic acid. A result is shown in the following table 4.

[0038]

[Table 4]

表 4	
サンプル	バリヤ改良因子
未処理基板	1. 0 (定義による)
市販のポリアクリル酸	1. 1 ± 0. 1
実施例 3 のコーティング	7. 2 ± 0. 9

[0039]

In the coated nylon board, the lap shear test (lap shear test) was carried out like next. Two opposed faces of the coated nylon board were piled up, the joint which covers 1-cm² was formed, and the substrate was stiffened in 60 minutes and under the weight of 2 kg at 70 **. Next, the adhesive strength of each joint was determined by recording the maximum load which pulled apart the substrate the speed for 5-mm/using the tension gauge (tensilometer) (Instron), and reached before destroying. The coated substrate bore the maximum load of 74**11Ncm⁻² before destruction. The comparison joint manufactured from the nylon which is not coated did not show the adhesion characteristic at all.

[0040]

Working example 4

The method of working example 2 was repeated using 1H, 1H, and 2H-perfluoro-1-octene (CF₃(CF₂)₅CH=CH₂) as a glass substrate and a coating formation material.

[0041]

x linear-light electronic spectroscopic analysis, FTIR analysis, and angle-of-contact measurement (using water and Deccan) were carried out according to above-mentioned working example 1. A result is shown in the following table 5. It was shown by XPS and FTIR analysis that glass substrate coating is abundant in CF₂ and CF₃. Working example 1 determined water and the angle of contact over Deccan.

[0042]

[Table 5]

表 5						
	XPS分析	接触角 (水)			接触角 (デカン) (°)	
		%C	%F	%O		
理論		38.1	61.9	—	—	
実施例4のコーティング		38.0	60.0	2.1	118.9±3.0	
					61.1±2.2	

[0043]

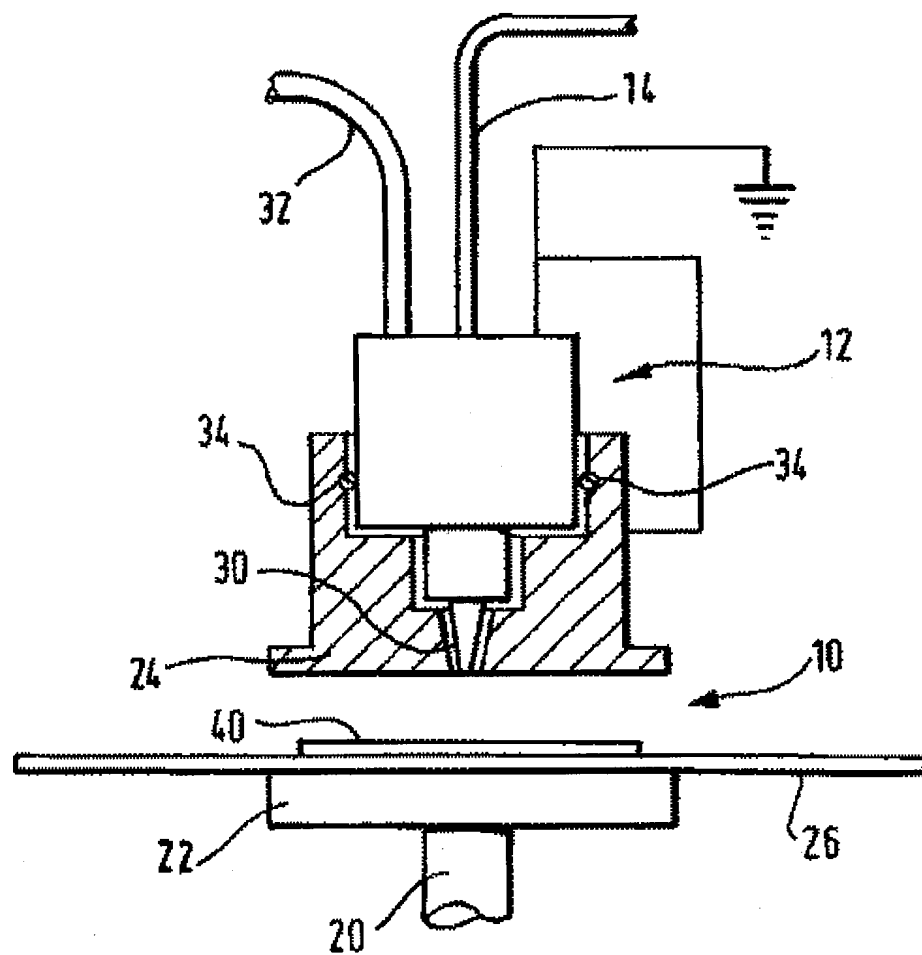
It was shown by the measurement result of the angle of contact that the glass substrate was substantially made hydrophobicity and sparse oiliness by coating.

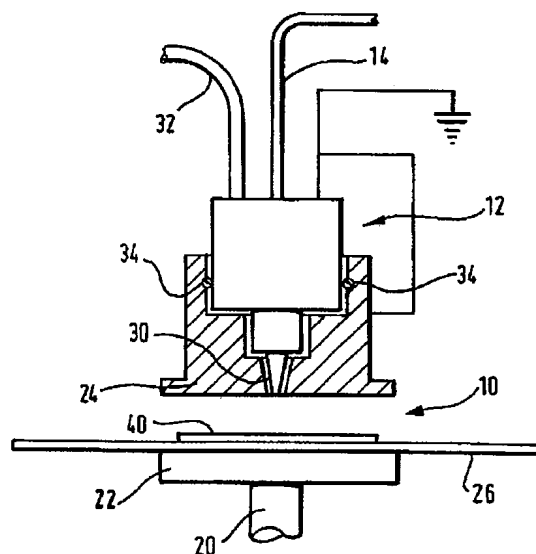
[Brief Description of the Drawings]

[Drawing 1]

It is a figure for describing the embodiment of the device in this invention.

[Translation done.]





【特許請求の範囲】**【請求項 1】**

基板上にコーティングを形成する方法であって、噴霧液体および／または固体コーティング形成材料を大気圧プラズマ放電および／またはそれから発生するイオン化ガス流中に導入することと、前記基板を前記噴霧コーティング形成材料へさらすこととを含む方法。

【請求項 2】

前記コーティング形成材料は、直接注入によって導入される請求項 1 に記載の方法。

【請求項 3】

前記コーティング形成材料は、ケイ素含有材料である請求項 1 または 2 に記載の方法。

【請求項 4】

前記コーティング形成材料は、ジメチルシロキサン、およびケイ素－水素結合を有するシロキサンから選択される請求項 3 に記載の方法。

【請求項 5】

前記プラズマは、酸素含有雰囲気中で発生される請求項 1 ないし 4 のいずれか 1 項に記載の方法。

【請求項 6】

前記コーティング形成材料は、有機材料または有機金属材料である請求項 1 または 2 に記載の方法。

【請求項 7】

前記コーティング形成材料は、アクリル酸およびペルフルオロアルケンから選択される請求項 6 に記載の方法。

【請求項 8】

前記基板は、金属、セラミック、プラスチック、繊維または不織繊維、天然繊維、合成繊維、セルロース系材料、および粉末を含む請求項 1 ないし 7 のいずれか 1 項に記載の方法。

【請求項 9】

前記コーティングは、基板の接着、剥離、ガスバリア、水分バリア、電気および熱伝導性、光学、誘電、親水性、疎水性、および／または疎油性特性を増大させる請求項 1 ないし 8 のいずれか 1 項に記載の方法。

【請求項 10】

請求項 1 ないし 9 のいずれか 1 項に記載の方法に従って多層コーティングを有する基板を製造する方法であって、それにより、前記基板に大気圧プラズマグロー放電に繰り返し通過させるか、または前記基板を一連の大気圧グロー放電チャンバに通過させることによって、前記コーティングが施される方法。

【請求項 11】

ポリマー形成材料を重合させる方法であって、該ポリマー形成材料を噴霧することと、噴霧ポリマー形成材料を大気圧プラズマ放電へさらすこととを含む方法。

【請求項 12】

前記噴霧液体および／または固体コーティング形成材料の化学特性は、結果として形成されるコーティングにおいて実質的に保持される請求項 1 ないし 4、6 または 7 に記載の方法。

【請求項 13】

前記基板は、リールまたはリール式装置によって連続的にコーティングされる請求項 1 ないし 12 のいずれか 1 項に記載の方法。

【請求項 14】

前記基板は、コーティング形成材料の導入の前にプラズマ暴露によって前処理される請求項 1 ないし 13 のいずれか 1 項に記載の方法。

【請求項 15】

前記基板上に形成された前記コーティングは、プラズマへの暴露によって後処理される請求項 1 ないし 14 のいずれか 1 項に記載の方法。

【請求項 16】

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前記プラズマは、大気圧グロー放電によって印加される請求項 1 4 または 1 5 に記載の方法。

【請求項 1 7】

酸素含有材料がプラズマへ添加される請求項 1 6 に記載の方法。

【請求項 1 8】

前記酸素含有材料は、酸素ガスおよび水の群から選択される請求項 1 7 に記載の方法。

【請求項 1 9】

基板上にコーティングを形成するための装置であって、使用時に前記基板がその内部に配置される、大気圧プラズマグロー放電を発生させるための手段と、プラズマ放電内に噴霧コーティング形成材料を提供するための噴霧器と、コーティング形成材料を該噴霧器へ供給するための手段とを含む装置。

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【請求項 2 0】

前記噴霧器は、超音波ノズルである請求項 1 9 に記載の装置。

【請求項 2 1】

前記基板は、前記基板の連続コーティングを可能にするために、リールまたはリール式装置へ固定される請求項 1 9 または 2 0 に記載の装置。

【請求項 2 2】

請求項 1 ないし 1 8 のいずれか 1 項に記載の方法によって調製されるコーティング基板。

【請求項 2 3】

前記噴霧液体および／または固体コーティング形成材料の化学特性は、得られたコーティングにおいて保持される請求項 2 2 に記載のコーティング基板。

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【請求項 2 4】

積層の接着剤、酸素および／または水分バリアとして、あるいは有機発光ダイオードデバイスにおける、請求項 1 ないし 1 8 のいずれか 1 項に記載の方法により形成されるコーティング基板の使用。

【発明の詳細な説明】

【0 0 0 1】

本発明は基板上にコーティングを形成する方法に関し、特に、大気圧プラズマ放電を用いて基板上にコーティングを形成する方法、ポリマー形成材料を重合させる方法、さらに、基板上にコーティングを形成するための装置に関する。

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【0 0 0 2】

例えば、基板を腐食から保護するため、酸化に対するバリアを提供するため、他の材料との接着性を改良するため、表面活性を増大させるため、および基板の生物医学的適合性のために種々の理由のために基板をコーティングすることができる。基板表面を修飾またはコーティングするために一般的に使用される方法は、基板を反応容器内に置いて、プラズマ放電を施すことである。このような処理の多くの例が当該技術で知られており、例えば、米国特許第 5, 8 7 6, 7 5 3 号は固体表面へ標的材料を付着させるためのプロセスを開示し、このプロセスは、低出力可変デューティサイクルパルスプラズマ蒸着によって表面に炭素系化合物を付加することを含む。また、欧州公開第 0 8 9 6 0 3 5 号は基板およびコーティングを有する装置を開示し、少なくとも 1 つの有機化合物またはモノマーを含む気体のプラズマ重合によって基板にコーティングが施される。本出願の最初の優先日後に始めて公開された独国特許第 1 9 9 2 4 1 0 8 号は、基板上に染料および腐食防止剤をコーティングするためのプロセスを記載する。プロセスには、基板上に液体薄膜コーティングを施し、続いてプラズマポリマー保護コーティングを施すことが包含される。プラズマポリマーコーティングは、気体モノマーおよび低圧プラズマを用いて形成される。

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【0 0 0 3】

しかしながら、このようなプラズマ表面処理では基板を減圧条件下に置くことが必要とされ、したがって、真空チャンバが必要とされる。通常のコーティング形成ガス圧は、 $5 \text{ N m}^{-2} \sim 25 \text{ N m}^{-2}$ ($1 \text{ 気圧} = 1.01 \times 10^5 \text{ N m}^{-2}$ を参照) の範囲である。減圧を必要とする結果として、表面処理は高価であると共にバッチ処理に限定され、コーティ

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ング形成材料は、減圧条件を保持するために気体または蒸気の形態でなければならない。

【0004】

本発明者らは、大気圧プラズマ放電と、噴霧液体および／または固体コーティング形成材料との組み合わせを用いて、基板表面プラズマ処理の上述の不利な状態を克服することができることを発見した。

【0005】

従って、本発明によると、基板上にコーティングを形成する方法が提供され、上記方法は、噴霧液体および／または固体のコーティング形成材料を大気圧プラズマ放電および／またはそれから発生するイオン化ガス流中に導入することと、上記基板を噴霧コーティング形成材料へさらすこととを含む。

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【0006】

本発明によるコーティング形成材料は、例えば、薄膜を成長させるため、または現存の表面を化学的に修飾するために使用することができる材料を含む、任意の適切なコーティングを作製するために使用することができる材料であると理解されるべきである。

【0007】

また本発明はポリマー形成材料を重合させる方法も提供し、上記方法は、ポリマー形成材料を噴霧することと、上記ポリマー形成材料を大気圧プラズマ放電へさらすこととを含む。

【0008】

本発明は、基板上にコーティングを形成するための装置をさらに提供し、上記装置は、使用時に上記基板がその内部に配置される、大気圧プラズマ放電を発生させるための手段と、プラズマ放電内に噴霧コーティング形成材料を提供するための噴霧器と、上記噴霧器へコーティング形成材料を供給するための手段とを含む。

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【0009】

大気圧プラズマグロー放電を発生させるための従来のどの手段も本発明において使用でき、例えば、大気圧プラズマジェット、大気圧マイクロ波グロー放電および大気圧グロー放電などが挙げられる。通常は、このような手段は、ペニングイオン化メカニズムにより大気圧で均一なグロー放電を発生させるために、ヘリウム希釈剤および高周波数（例えば、 $>1\text{ kHz}$ ）電源を使用することができる（例えば、Kanazawaら, J. Phys. D: Appl. Phys. 1988, 21, 838、Okazakiら, Proc. Jpn. Symp. Plasma Chem. 1989, 2, 95、Kanazawaら, Nuclear Instruments and Methods in Physical Research 1989, B37/38, 842、およびYokoyamaら, J. Phys. D: Appl. Phys. 1990, 23, 374を参照）。

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【0010】

コーティング形成材料は、例えば、超音波ノズルなどの従来のどの手段を用いて噴霧されてもよい。噴霧器は、 $10\sim100\text{ }\mu\text{m}$ の大きさのコーティング形成材料滴を生成するのが好ましく、更に好ましくは $10\sim50\text{ }\mu\text{m}$ である。本発明で使用するのに適切な噴霧器は、Sono-Tek Corporation, Milton, New York, USAからの超音波ノズルである。本発明の装置は、例えば、装置が2つの異なるコーティング形成材料から基板上にコポリマーコーティングを形成するのに使用される場合や、モノマーが非混和性であるかまたは異なる相に存在する、例えば、第1の相が固体で第2の相が気体または液体である場合に、特に役に立つ複数の噴霧器を含むことができる。

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【0011】

本発明は、多くの異なるタイプの基板コーティングを形成するために使用することができる。基板上に形成されるコーティングのタイプは、使用されるコーティング形成材料（単数または複数）によって決定され、本発明の方法は、基板表面上にコーティング形成モノマー材料（単数または複数）を重合（共重合）させるために使用されてもよい。コーティング形成材料は、有機もしくは無機の、固体、液体または気体、あるいはそれらの混合物

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であり得る。適切な有機コーティング形成材料としては、カルボン酸エステル、メタクリル酸エステル、アクリル酸エステル、スチレン、メタクリロニトリル、アルケンおよびジエン、例えば、メタクリル酸メチル、メタクリル酸エチル、メタクリル酸プロピル、メタクリル酸ブチル、ならびに、他のメタクリル酸アルキルおよび対応するアクリル酸エステル、（有機官能性メタクリル酸エステルおよびアクリル酸エステルを含む（メタクリル酸グリシジル、メタクリル酸トリメトキシシリルプロピル、メタクリル酸アリル、メタクリル酸ヒドロキシエチル、メタクリル酸ヒドロキシプロピル、メタクリル酸ジアルキルアミノアルキル、およびメタ（アクリル）酸フルオロアルキルを含む））メタクリル酸、アクリル酸、フマル酸およびエステル、イタコン酸（およびエステル）、無水マレイン酸、スチレン、 α -メチルスチレン、ハロゲン化アルケン、例えば、塩化ビニルおよびフッ化ビニルなどのハロゲン化ビニル、およびフッ素化アルケン、例えばペルフルオロアルケン、アクリロニトリル、メタクリロニトリル、エチレン、プロピレン、アリルアミン、ハロゲン化ビニリデン、ブタジエン、N-イソプロピルアクリルアミドなどのアクリルアミド、メタクリルアミド、エポキシ化合物、例えば、グリシドキシプロピルトリメトキシシラン、グリシドール、スチレンオキシド、ブタジエンモノオキシド、エチレングリコール、ジグリシジルエーテル、メタクリル酸グリシジル、ビスフェノール A ジグリシジルエーテル（およびそのオリゴマー）、ビニルシクロヘキセンオキシド、ピロールおよびチオフェンならびにそれらの誘導体などの電導性ポリマー、ならびに例えばジメチルアリルホスホネートなどのリン含有化合物が挙げられる。適切な無機コーティング形成材料としては、コロイド金属を含む金属および金属酸化物が挙げられる。また、有機金属化合物も適切なコーティング形成材料であり、チタン酸塩、スズアルコキシド、ジルコン酸塩、ならびにゲルマニウムおよびエルビウムのアルコキシドなどの金属アルコキシドが含まれる。しかしながら、本発明者らは、ケイ素含有材料を含むコーティング形成組成物を用いて基板にシリカベースまたはシロキサンベースのコーティングを提供する際に、本発明が特に役に立つことを発見した。本発明の方法で使用するのに適切なケイ素含有材料としては、シラン類（例えば、シラン、アルキルハロシラン、アルコキシシラン）、ならびに直鎖（例えば、ポリジメチルシロキサン）および環状シロキサン（例えば、オクタメチルシクロテトラシロキサン）（有機官能性直鎖ならびに環状シロキサン（例えば、Si-H含有、ハロ官能性、およびハロアルキル官能性の直鎖および環状シロキサン、例えばテトラメチルシクロテトラシロキサンおよびトリ（モノフルオロブチル）トリメチルシクロトリシロキサンを含む）が挙げられる。例えば、特定の必要性に対して基板コーティングの物理特性を適合させるために、異なるケイ素含有材料の混合物を使用してもよい（例えば、熱特性、屈折率などの光学特性、および粘弾性特性）。

【0012】

更に、酸化条件下では、本発明の方法を使用して、基板上に酸素含有コーティングを形成することができる。例えば、噴霧ケイ素含有コーティング形成材料から、基板表面にシリカベースのコーティングを形成することができる。還元条件下では、本発明を使用して酸素を含まないコーティングを形成でき、例えば、噴霧ケイ素含有コーティング形成材料から、炭化ケイ素ベースのコーティングを形成することができる。

【0013】

また、例えば、希ガス、空気、水素、窒素およびアンモニアなどの酸素以外の気体を含むプラズマ発生条件を用いることもできる。窒素含有雰囲気中では窒素が基板表面に結合でき、窒素および酸素含有雰囲気中ではナイトレートが基板表面上に結合および／または形成することができる。このような気体は、コーティング形成物質へさらす前に基板表面を前処理するためにも使用することができる。例えば、基板の酸素含有プラズマ処理は、施されたコーティングとの接着の改良を提供することができる。酸素含有プラズマは、酸素含有材料を酸素ガスまたは水などのプラズマへ導入することによって発生されている。更に、基板上に形成されたコーティングは、種々のプラズマ条件で後処理されてもよい。例えば、シロキサン由来のコーティングは、さらに、酸素含有プラズマ処理によって酸化されてもよい。酸素含有プラズマは、酸素含有材料を酸素ガスまたは水などのプラズマ

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へ導入することによって発生されている。

【0014】

従来技術を越える本発明の利点は、本発明の方法が大気圧条件下で行われるために、液体と固体の両方の噴霧コーティング形成材料を使用して、基板コーティングを形成することができることである。さらには、コーティング形成材料は、キャリアガスの非存在下で、プラズマ放電または結果として発生する流れの中に導入することができる、すなわち、例えば直接注入によって直接導入することができ、それによって、コーティング形成材料はプラズマ中に直接注入される。

【0015】

上述のように、本発明者らは、ケイ素含有材料を用いて基板上にシリカベースおよびシロキサンベースのコーティングを形成するために本発明が特に役に立つことを発見した。例えば酸素含有雰囲気などの酸化条件下では、噴霧ケイ素含有材料から基板表面にシリカベースのコーティングを形成することができるが、非酸化条件下では、ケイ素含有モノマーの噴霧から基板表面に例えば直鎖、分枝または樹脂状シロキサンポリマーなどのシロキサンポリマーを形成することができる。有機およびケイ素含有モノマーの混合物の使用によって、基板表面にシロキサン有機ポリマーを形成することができる。さらに、シリカベースのコーティングを基板表面に形成し、次にこれを、例えば有機またはシロキサンポリマーなどの更なる材料によってコーティングしてもよい。例えば、シロキサンが有機ポリマーと混合され、該混合物から基板が形成される場合、有機ポリマーとシロキサンの間の表面エネルギーの相違のために、シロキサンは基板の有機ポリマー本体表面へ移動することができる。次にこの基板に大気圧プラズマ処理が施されると、基板表面のシロキサンは酸化されて、シリカベースのコーティングを形成する。このシリカベースのコーティングには、次に、噴霧ケイ素含有モノマーの存在下で大気圧プラズマ処理を更に施すことによって本発明に従う処理が行われ、シロキサンコーティングがその上に形成される。しかしながら、本発明は、例えば、ポリアクリル酸またはペルフルオロ有機コーティングなどの有機コーティングを基板上に形成するためにも有用である。

【0016】

コーティングされる基板は、例えば金属、セラミック、プラスチック、シロキサン、織または不織繊維、天然繊維、合成繊維、セルロース系材料および粉末などの任意の材料を含むことができる。しかしながら、基板のサイズは、大気圧プラズマ放電が発生される容積の寸法、すなわちプラズマ発生手段の電極間の距離によって制限される。典型的なプラズマ発生装置では、プラズマは、5 mmから50 mm、例えば12 mmから25 mmの間隙内で発生される。したがって、本発明は、薄膜、繊維および粉末をコーティングするために、特に役に立つ。

【0017】

本発明の方法によってコーティングされる基板は種々の効用を有することができる。例えば、酸化雰囲気中で発生されるシリカベースのコーティングは、基板のバリヤおよび／または拡散特性を強化でき、基板表面へ更なる材料が接着する能力を高めることができる。ハロ官能性有機またはシロキサンコーティング（例えば、ペルフルオロアルケン）は、基板の疎水性、疎油性、燃料および土壌耐性、および／または剥離特性を増大することができる。ポリジメチルシロキサンコーティングは基板の耐水性および剥離特性を強化でき、繊維の手触りの柔らかさを高めることができる。ポリアクリル酸重合体コーティングは、基板表面への接着を促進するための接着層としてまたは積層構造の一部として使用することができる。コーティングにコロイド金属種を含有させると、基板へ表面伝導性が提供されるか、あるいはその光学特性が高められる。ポリチオフェンおよびポリピロールは、金属基板に耐腐食性も提供することができる導電性高分子コーティングを与える。

【0018】

プラズマ処理を含むプロセスを用いて基板をコーティングする場合に発生しやすい1つの主要な問題は、コーティングの形成に使用される材料の化学特性が損失されるかもしれないことである。したがって、本発明の主要な利点は、コーティング形成材料の化学特性が

、形成されたコーティングにおいて実質的に保持されることである。例えば、コーティング形成材料としてアクリル酸が使用される場合、カルボン酸の官能性は、形成されたコーティングにおいて実質的に保持される。

【0019】

また本発明は、上記のプロセスによって多層コーティングを有する基板を製造する方法を提供する。この場合、基板に大気圧プラズマグロー放電を繰返し通過させるたびにコーティング層が施される。好ましくは、このような場合、基板は、オープンリール式プロセスとして大気圧プラズマグロー放電を通して輸送されることによって連続的にコーティングでき、ここで、基板全体がグロー放電内で所定の滞留時間を有することを保証するために、基板は一定の速度で第1のリールからグロー放電を通過して第2のリール上へ移動する。各基板はグロー放電を1回または複数回通過されることができ、これにより、第1の通過の第1の、即ち供給リールは第2の通過では基板回収リールになり、第1の通過の基板回収リールは次に第2の通過では供給リールであり、2つのリールは各通過の最後に交換される。あるいは、基板は一連の大気圧グロー放電チャンバを通過させられてもよい。

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【0020】

本発明に従ってコーティングされた基板のコーティングの好ましい用途には、積層体の接着剤、例えば食品パッケージング用途のための酸素および／または水分のバリヤ、ならびに例えばフラットパネルディスプレイなどにおける有機発光ダイオードデバイスの中または上の構成要素としての用途が含まれる。

【0021】

本発明をここに、添付図面を参照して詳細に説明する。

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【0022】

図1に示される本発明に従う装置は大気圧プラズマ放電を発生させるための手段（概略的に10で示される）および噴霧器（概略的に12で示される）を備えており、噴霧器12は、コーティング形成材料を噴霧器12へ供給するためのシリンジポンプ14へ接続される。放電を発生させるための手段10には、12mm離間された2つのアルミニウム電極22および24にわたって供給される高電圧15kHzのac電源20が含まれ、下部ライブ電極（live electrode）22は、ガラス誘電プレート26によって遮断される。噴霧器12はSonotek[®] 8700-120超音波ノズル30を有し、Sonotek[®] 06-05108広帯域超音波発生器32へ接続される。噴霧器12はオリング34上でアース電極24内に固定される。コーティングされる基板40は、電極22および24間のガラス誘電プレート26上に配置される。

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【0023】

図1を参照して上文で説明した装置を、下記の全ての手順のために使用した。

(* Sonotek Corporation, Milton, New York 12547, USA)

【0024】

実施例1

イソプロピルアルコールおよびシクロヘキサンの1:1混合物中で一片のポリエチレン薄膜基板を超音波洗浄し、ガラスプレート上に配置した。残留ガスを排気した後、流速1900sccmおよび圧力 $1.02 \times 10^5 \text{ Nm}^{-2}$ でプラズマ放電ガスを導入した。ヘリウムおよび99%ヘリウム/1%酸素混合物の2種の放電ガスを使用した。10分間パージした後、シリンジポンプ14のスイッチを入れ、コーティング形成材料を $3 \times 10^{-5} \text{ ml s}^{-1}$ の速度で流動させた。オクタメチルシクロテトラシロキサン（以下、「D₄」と称する）およびテトラメチルシクロテトラシロキサン（以下、「D₄H」と称する）の2種のコーティング形成材料を使用した。コーティング形成材料が超音波ノズルへ到達したら、コーティング形成材料の噴霧を開始するために超音波発生器のスイッチを入れ（2.5W）、電極に1.5kVを印加することによって、大気圧プラズマ放電を引き起こした。コーティング形成材料の蒸着を10分間続行させた後、基板を取り出し、減圧下に20分間配置して不安定材料を除去した。

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【0025】

上記手順の結果は以下の表1に示される。x線光電子分光分析 (K r a t o s E S 3 0 0) を用いて基板表面の元素分析を実行し、分光光度計 (A q u i l a I n s t r u m e n t s の n k d - 6 0 0 0) を用いて膜厚を決定した。脱イオン水の定着性 $2 \mu l$ の液滴を使用し、ビデオキャプチャ装置 (A S T P r o d u c t s の V C A 2 5 0 0 X E) を用いて接触角測定を行った。

【0026】

また、質量分析計を用いて、基板表面の気体透過度測定も行った。結果は表2に示される。バリアの改良因子は、[コーティングされた基板の気体透過] / [リファレンスサンプルの気体透過] として計算される。

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【0027】

【表1】

【 0 0 2 8 】
【 表 2 】

表 1								
サンプル	XPS分析				接触角 (°)	蒸着速度 (nm s^{-1})	コーティング厚 (nm)	
	%C	%O	%Si	%SiO _x				
D ₄ 理論	50	25	25	0	—	—	—	
D ₄ 100% He	43.3	29.3	25.8		107.8*	28	279	
D ₄ 1% O ₂	25.5	48.5	26.0	74.4	56.4	29	286	
D ₄ H理論	33.3	33.3	33.3	0	—	—	—	
D ₄ H 100%He	32.5	39.1	28.4		102.3	82		
D ₄ H1% O ₂	9.2	61.4	29.5	81.5	ウェット	244		

*清浄なポリエチレンは接触角が105.8°である。

表 2	
サンプル	バリア改良因子
清浄ポリエチレン	1.0 (定義による)
D ₄ , 100% He	0.9
D ₄ , 1% O ₂	6.8
D ₄ H, 100% He	0.9
D ₄ H, . 1% O ₂	4.5

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【0029】

基板表面のATR-FTIR研究は、D₄ および D₄ Hコーティング形成材料の開環重合が発生して、基板表面にポリシロキサンが形成されたことを示した。特に、後者に関するATR-FTIR研究によって、ポリシロキサンコーティングは、D₄ HのSi-H官能性の多くを保持することが示された。

【0030】

上記のようにガラス表面に調製したコーティングのNMR研究によって、D₄ および D₄ Hコーティング形成材料の重合で基板表面に形成されたポリシロキサンは、二価の(CH₃)₂SiO₂/2 単位および三価のCH₃SiO₃/2 単位を含む、すなわちポリシロキサンは樹脂状であることが示された。

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【0031】

実施例 2

ガラス基板、コーティング形成材料としてアクリル酸、および放電ガスとしてヘリウムだけを使用して、上記実施例 1 の方法を繰り返した。分析の前に基板からコーティングを取り外した。

【0032】

コーティングのFTIRおよび固体NMR分析では、アクリル酸が重合してポリアクリル酸が形成されたことを確認した。FTIRおよびNMRデータはいずれも、不飽和C=C結合の消費を示した。

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【0033】

実施例 3

ナイロンおよびポリエチレン基板を用いて、実施例 2 の方法を繰り返した。

【0034】

市販のポリアクリル酸でのコーティングのFTIR分析の比較によって、アクリル酸コーティング形成材料が重合して、基板表面にポリアクリル酸コーティングが形成されたことを確認した。

【0035】

上記の実施例 1 によって x 線光電子分光分析、膜厚分析、および接触角測定を実施した。結果を以下の表 3 に示す。

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【0036】

【表 3】

表3					
	XPS分析			接触角 (°)	蒸着速度 (nm s^{-1})
	%C	%O	%CO ₂ H		
理論	60.0	40.0	33.3	—	—
市販のポリ アクリル酸	63.3	36.7	29.9	ウェット	—
実施例3の コーティング	62.6	37.4	26.4	ウェット	231±95

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【0037】

質量分析によって、コーティングされたポリエチレン薄膜を通る気体輸送を決定した。上記実施例1により計算されるバリア改良因子は、未処理のポリエチレン基板および市販のポリアクリル酸よりも大きかった。結果を以下の表4に示す。

【0038】

【表4】

表4	
サンプル	バリア改良因子
未処理基板	1.0 (定義による)
市販のポリアクリル酸	1.1±0.1
実施例3のコーティング	7.2±0.9

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【0039】

コーティングされたナイロン基板において次のようにラップせん断試験 (lap shear test) を実施した。コーティングされたナイロン基板の2つの対向面を重ね合わせて、 1 cm^2 を被覆するジョイントを形成し、70℃で60分間、2kgの重量下で基板を硬化させた。次に、張力計 (tensile meter) (Instron) を用いて5mm/分の速度で基板を引き離し、破壊する前に達した最大負荷を記録することによって、各ジョイントの接着強度を決定した。コーティングされた基板は、破壊の前に、 $74 \pm 11\text{ N cm}^{-2}$ の最大負荷に耐えた。コーティングされていないナイロンから製造した比較ジョイントは接着特性を全く示さなかった。

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【0040】

実施例4

ガラス基板、およびコーティング形成材料として1H、1H、2H-ペルフルオロ-1-オクテン ($\text{CF}_3(\text{CF}_2)_5\text{CH}=\text{CH}_2$) を用いて、実施例2の方法を繰り返した。

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【0041】

上記の実施例1によってx線光電子分光分析、FTIR分析および接触角測定 (水およびデカンを用いて) を実施した。結果を以下の表5に示す。XPSおよびFTIR分析により、ガラス基板コーティングは CF_2 および CF_3 が豊富であることが示された。水およびデカンに対する接触角は実施例1によって決定した。

【0042】

【表5】

表 5					
	XPS分析	接触角 (水)			接触角 (デカン) (°)
		%C	%F	%O	
理論		38.1	61.9	—	—
実施例4のコーティング		38.0	60.0	2.1	118.9±3.0
					61.1±2.2

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【0043】

接触角の測定結果では、ガラス基板はコーティングによって実質的に疎水性および疎油性にされたことが示された。

【図面の簡単な説明】

【図1】

本発明における装置の実施形態を説明するための図である。

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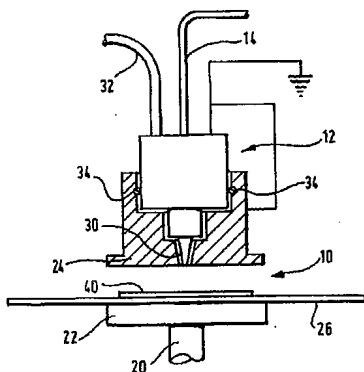
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[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR FORMING A COATING



(57) Abstract: A method for forming a coating on a substrate using an atmospheric pressure plasma discharge. The method comprises introducing an atomised liquid and/or solid coating-forming material into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom, and exposing the substrate to the atomised coating-forming material. The application also describes a method for polymerising a polymer forming material, and further to apparatus for forming a coating on a substrate.

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METHOD AND APPARATUS FOR FORMING A COATING

[0001] The present invention relates to a method for forming a coating on a substrate, in particular a method for forming a coating on a substrate using an atmospheric pressure plasma discharge, a method for polymerising a polymer forming material, and further to apparatus for forming a coating on a substrate.

[0002] Substrates may be coated for a variety of reasons, for example to protect the substrate from corrosion, to provide a barrier to oxidation, to improve adhesion with other materials, to increase surface activity, and for reasons of biomedical compatibility of the substrate. A commonly used method for modifying or coating the surface of a substrate is to place the substrate within a reactor vessel and subject it to a plasma discharge. Many examples of such treatment are known in the art; for example, US patent number 5,876,753 discloses a process for attaching target materials to a solid surface which process includes affixing carbonaceous compounds to a surface by low power variable duty cycle pulsed plasma deposition, and EP-A-0896035 discloses a device having a substrate and a coating, wherein the coating is applied to the substrate by plasma polymerisation of a gas comprising at least one organic compound or monomer. DE 19924108, which was first published after the initial priority date of the present application, describes a process for coating dyestuffs and corrosion inhibitors onto substrates. The process involves the application of a liquid film coating onto a substrate and a subsequent plasma polymer protective coating. The plasma polymer coating is formed using gaseous monomers and low pressure plasma.

- 2 -

- [0003] However, such plasma surface treatments require the substrate to be under conditions of reduced pressure, and hence require a vacuum chamber. Typical coating-forming gas pressures are in the range 5 to 25 Nm⁻² (cf. 1 atmosphere = 1.01x10⁵ Nm⁻²). As a result of the requirement for reduced pressure, surface treatments are expensive, are limited to batch treatments, and the coating-forming materials must be in gaseous and/or vapour form in order to maintain conditions of reduced pressure.
- 10 [0004] The present inventors have found that the abovementioned disadvantages of substrate surface plasma treatment can be overcome using a combination of an atmospheric pressure plasma discharge and an atomised liquid and/or solid coating forming material.
- 15 [0005] Thus, according to the present invention there is provided a method for forming a coating on a substrate, which method comprises introducing an atomised liquid and/or solid coating-forming material into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting
- 20 therefrom, and exposing the substrate to the atomised coating-forming material.
- [0006] It is to be understood that the coating forming material in accordance with the present invention is a material which can be used to make any appropriate coating, including, for example, a material which can be used to grow
- 25 a film or to chemically modify an existing surface.
- [0007] The present invention also provides a method for polymerising a polymer-forming material, which method comprises atomising the polymer-forming material, and
- 30 exposing the polymer-forming material to an atmospheric pressure plasma discharge.

[0008] The present invention further provides apparatus for forming a coating on a substrate, which apparatus comprises means for generating an atmospheric pressure plasma discharge within which, in use, the substrate is placed, an atomiser for providing an atomised coating-forming material within the plasma discharge, and means for supplying a coating forming material to the atomiser.

[0009] Any conventional means for generating an atmospheric pressure plasma glow discharge may be used in the present invention, for example atmospheric pressure plasma jet, atmospheric pressure microwave glow discharge and atmospheric pressure glow discharge. Typically such means will employ a helium diluents and a high frequency (e.g. > 1kHz) power supply to generate a homogeneous glow discharge at atmospheric pressure via a Penning ionisation mechanism, (see for example, Kanazawa et al, J.Phys. D: Appl. Phys. 1988, 21, 838, Okazaki et al, Proc. Jpn. Symp. Plasma Chem. 1989, 2, 95, Kanazawa et al, Nuclear Instruments and Methods in Physical Research 1989, B37/38, 842, and Yokoyama et al., J. Phys. D: Appl. Phys. 1990, 23, 374).

[0010] The coating-forming material may be atomised using any conventional means, for example an ultrasonic nozzle. The atomiser preferably produces a coating-forming material drop size of from 10 to 100µm, more preferably from 10 to 50µm. Suitable atomisers for use in the present invention are ultrasonic nozzles from Sono-Tek Corporation, Milton, New York, USA. The apparatus of the present invention may include a plurality of atomisers, which may be of particular utility, for example, where the apparatus is to be used to form a copolymer coating on a substrate from two different coating-forming materials, where the monomers are immiscible

- 4 -

or are in different phases, e.g. the first is a solid and the second is gaseous or liquid.

- [0011] The present invention may be used to form many different types of substrate coatings. The type of coating which is formed on the substrate is determined by the coating-forming material(s) used, and the present method may be used to (co)polymerise coating-forming monomer material(s) onto the substrate surface. The coating-forming material may be organic or inorganic, solid, liquid or gaseous, or mixtures thereof. Suitable organic coating-forming materials include carboxylates, methacrylates, acrylates, styrenes, methacrylonitriles, alkenes and dienes, for example methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, and other alkyl methacrylates, and the corresponding acrylates, including organofunctional methacrylates and acrylates, including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, and fluoroalkyl (meth)acrylates, methacrylic acid, acrylic acid, fumaric acid and esters, itaconic acid (and esters), maleic anhydride, styrene, α -methylstyrene, halogenated alkenes, for example, vinyl halides, such as vinyl chlorides and vinyl fluorides, and fluorinated alkenes, for example perfluoroalkenes, acrylonitrile, methacrylonitrile, ethylene, propylene, allyl amine, vinylidene halides, butadienes, acrylamide, such as N-isopropylacrylamide, methacrylamide, epoxy compounds, for example glycidoxypropyltrimethoxysilane, glycidol, styrene oxide, butadiene monoxide, ethyleneglycol diglycidylether, glycidyl methacrylate, bisphenol A diglycidylether (and its oligomers), vinylcyclohexene oxide, conducting polymers such

- 5 -

- as pyrrole and thiophene and their derivatives, and phosphorus-containing compounds, for example dimethylallylphosphonate. Suitable inorganic coating-forming materials include metals and metal oxides, including
- 5 colloidal metals. Organometallic compounds may also be suitable coating-forming materials, including metal alkoxides such as titanates, tin alkoxides, zirconates and alkoxides of germanium and erbium. However, the present inventors have found that the present invention has
- 10 particular utility in providing substrates with silica- or siloxane-based coatings using coating-forming compositions comprising silicon-containing materials. Suitable silicon-containing materials for use in the method of the present invention include silanes (for example, silane,
- 15 alkylhalosilanes, alkoxysilanes) and linear (for example, polydimethylsiloxane) and cyclic siloxanes (for example, octamethylcyclotetrasiloxane), including organo-functional linear and cyclic siloxanes (for example, Si-H containing, halo-functional, and haloalkyl-functional linear and cyclic
- 20 siloxanes, e.g. tetramethylcyclotetrasiloxane and tri(nonfluorobutyl)trimethylcyclotrisiloxane). A mixture of different silicon-containing materials may be used, for example to tailor the physical properties of the substrate coating for a specified need (e.g. thermal properties,
- 25 optical properties, such as refractive index, and viscoelastic properties).
- [0012] In addition, under oxidising conditions the present method may be used to form an oxygen containing coating on the substrate. For example, silica-based
- 30 coatings can be formed on the substrate surface from atomised silicon-containing coating-forming materials. Under reducing conditions, the present method may be used to form

oxygen free coatings, for example, silicon carbide based coatings may be formed from atomised silicon containing coating forming materials.

[0013] Plasma generating conditions containing gases other than oxygen may also be employed, for example noble gases, air, hydrogen, nitrogen and ammonia. In a nitrogen containing atmosphere nitrogen can bind to the substrate surface, and in an atmosphere containing both nitrogen and oxygen, nitrates can bind to and/or form on the substrate surface. Such gases may also be used to pre-treat the substrate surface prior to exposure to the coating forming substance. For example oxygen containing plasma treatment of the substrate may provide improved adhesion with the applied coating. The oxygen containing plasma being generated by introducing oxygen containing materials to the plasma such as oxygen gas or water. Furthermore, the coating formed on the substrate may be post treated in a range of plasma conditions. For example, siloxane derived coatings may be further oxidised by oxygen containing plasma treatment. The oxygen containing plasma being generated by introducing oxygen containing materials to the plasma such as oxygen gas or water.

[0014] An advantage of the present invention over the prior art is that both liquid and solid atomised coating-forming materials may be used to form substrate coatings, due to the method of the present invention taking place under conditions of atmospheric pressure. Furthermore the coating-forming materials can be introduced into the plasma discharge or resulting stream in the absence of a carrier gas, i.e. they can be introduced directly by, for example, direct injection, whereby the coating forming materials are injected directly into the plasma.

- 7 -

[0015] As mentioned above, the present inventors have found particular utility of the present invention for forming silica- and siloxane-based coatings on substrates using silicon-containing materials. Under oxidising conditions, e.g. an oxygen containing atmosphere, silica-based coatings can be formed on the substrate surface from atomised silicon-containing materials, whereas under non-oxidising conditions a siloxane polymer, e.g. a linear, branched or resinous siloxane polymer, can be formed on the substrate surface from atomisation of a silicon-containing monomer. A siloxane-organic copolymer can be formed on the substrate surface by use of a mixture of organic and silicon-containing monomers. Furthermore, a silica-based coating may be formed on a substrate surface, which may in turn be coated by a further material, for example an organic or siloxane polymer. For example, when a siloxane is mixed with an organic polymer and a substrate formed from said mixture, the siloxane will migrate to the surface of the organic polymeric body of the substrate, due to the difference in surface energy between organic polymers and siloxanes. If this substrate is then subjected to atmospheric pressure plasma treatment, the siloxane on the surface of the substrate is oxidised to form a silica-based coating. This silica-based coating may then be subjected to treatment according to the present invention, by further subjecting it to atmospheric pressure plasma treatment in the presence of atomised silicon-containing monomers, to form a siloxane coating thereon. However, the present invention is also useful for forming an organic coating on a substrate, for example a polyacrylic acid or perfluoro-organic coating.

- 8 -

- [0016] The substrate to be coated may comprise any material, for example metal, ceramic, plastics, siloxane, woven or non-woven fibres, natural fibres, synthetic fibres cellulosic material and powder. However, the size of the substrate is limited by the dimensions of the volume within which the atmospheric pressure plasma discharge is generated, i.e. the distance between the electrodes of the means for generating the plasma. For typical plasma generating apparatus, the plasma is generated within a gap of from 5 to 50mm, for example 12 to 25mm. Thus, the present invention has particular utility for coating films, fibres and powders.
- [0017] Substrates coated by the method of the present invention may have various utilities. For example, a silica-based coating, generated in an oxidising atmosphere, may enhance the barrier and/or diffusion properties of the substrate, and may enhance the ability of additional materials to adhere to the substrate surface; a halo-functional organic or siloxane coating (e.g. perfluoroalkenes) may increase hydrophobicity, oleophobicity, fuel and soil resistance, and/or the release properties of the substrate; a polydimethylsiloxane coating may enhance water resistance and release properties of the substrate, and may enhance the softness of fabrics to touch; a polyacrylic acid polymeric coating may be used as an adhesive layer to promote adhesion to substrate surface or as part of laminated structure; the inclusion of colloidal metal species in the coatings may provide surface conductivity to the substrate, or enhance its optical properties. Polythiophene and polypyrrole give electrically conductive polymeric coatings which may also provide corrosion resistance on metallic substrates.

- 9 -

[0018] One major problem which tends to occur when coating substrates using a process involving plasma treatment is that the chemical properties of the material used to form the coating may be lost. It is therefore a major advantage of the present invention that the chemical properties of the coating forming material are substantially retained in the coating formed. For example, in the case where acrylic acid is used as the coating forming material, the carboxylic acid functionality is substantially maintained in the coating formed.

[0019] The present invention also provides a method of producing a substrate having a multi-layered coating by the above described processes. In this case a layer of the coating is applied upon each repeat pass of the substrate through the atmospheric plasma glow discharge. Preferably in such a case the substrate may be coated on a continuous basis by being transported through an atmospheric plasma glow discharge by way of a reel to reel process in which the substrate travels from a first reel, through the glow discharge and on to a second reel at a constant speed to ensure that all the substrate has a predetermined residence time within the glow discharge. Each substrate may be subjected to one or more passes through the glow discharge whereby the first or supply reel in the first pass becomes the substrate collecting reel in the second pass and the substrate collecting reel of the first pass in turn is the supply reel in the second pass, the two reels changing over at the end of each pass. Alternatively the substrate may be passed through a series of atmospheric glow discharge chambers.

- 10 -

[0020] Preferred uses of the coatings of the substrates coated in accordance with the present invention include lamination adhesives, oxygen and/or moisture barrier for example for food packaging applications and as a component
5 in or on organic light emitting diode devices in, for example, flat panel displays.

[0021] The present invention will now be illustrated in detail with reference to the accompanying drawing, in which
10 Figure 1 shows an embodiment of apparatus according to the present invention.

[0022] The apparatus according to the present invention shown in Figure 1 comprises means for generating an atmospheric pressure plasma discharge (generally designated
15 10), and an atomiser (generally designated 12) connected to a syringe pump 14 for supplying a coating forming material to the atomiser 12. The means for generating the discharge 10 includes a high voltage 15 kHz ac power supply 20, supplied across two aluminium electrodes 22 and 24 spaced
20 12mm apart, with the lower live electrode 22 shielded by a glass dielectric plate 26. The atomiser 12 includes a Sono-tek* 8700-120 ultrasonic nozzle 30, and is connected to a Sono-tek* 06-05108 broadband ultrasonic generator 32. The atomiser 12 is seated within the earth electrode 24 on an O-
25 ring 34. The substrate 40 to be coated is placed on the glass dielectric plate 26 between the electrodes 22 and 24.

[0023] The apparatus described hereinabove with reference to Figure 1 was used for all the procedures described hereinafter.

30 (* Sono-tek Corporation, Milton, New York 12547, USA).

Example 1

- [0024] A piece of polyethylene film substrate was ultrasonically washed in a 1:1 mixture of isopropyl alcohol and cyclohexane and was placed on the glass plate. After evacuation of residual gas, the plasma discharge gas was introduced at a flow rate of 1900 sccm and a pressure of 1.02×10^{-5} Nm². Two discharge gasses were used, helium and a 99% helium/1% oxygen mixture. After 10 minutes of purging, the syringe pump 14 was switched on and the coating-forming material was allowed to flow at a rate of 3×10^{-5} mls⁻¹. Two coating-forming materials were used, octamethylcyclotetrasiloxane (hereinafter referred to as "D₄") and tetramethylcyclotetrasiloxane (hereinafter referred to as "D₄H"). When the coating-forming material reached the ultrasonic nozzle, the ultrasonic generator was switched on (2.5 W) to initiate atomisation of the coating-forming material, and the atmospheric pressure plasma discharge was ignited by applying 1.5 kV across the electrodes. Deposition of the coating-forming material was allowed to proceed for 10 minutes, following which the substrate was removed and placed under vacuum for 20 minutes to remove any labile material.
- [0025] The results of the above procedure are shown in Table 1 below. X-ray photoelectron spectroscopic analysis (Kratos BS300) was used to perform elemental analysis of the substrate surface, and a spectrophotometer (Aquila Instruments nkd-6000) was used to determine film thickness. Contact angle measurements were made using video capture apparatus (AST Products VCA2500XB) using sessile 2µl droplets of deionised water.

[0026] Gas permeation measurements of the substrate surface were also taken using a mass spectrometer, and the results are shown in Table 2. The Barrier Improvement Factor is calculated as [coated substrate gas permeation]/[reference sample gas permeation].

Table 1							
Sample	XPS analysis				Contact	Deposition	Coating
	%C	%O	%Si	%SiO _x	Angle (°)	rate (nm s ⁻¹)	thickness (nm)
D ₁ theory	50	25	25	0	-	-	-
D ₁ 100% He	43.3	29.3	25.8		107.8*	28	279
D ₁ 1% O ₂	25.5	48.5	26.0	74.4	56.4	29	286
D ₁ H theory	33.3	33.3	33.3	0	-	-	-
D ₁ H 100%He	32.5	39.1	28.4		102.3	82	
D ₁ H 1% O ₂	9.2	61.4	29.5	81.5	wets	244	

* clean polyethylene has a contact angle of 105.8°

- 13 -

Table 2	
Sample	Barrier Improvement Factor
Clean polyethylene	1.0 (by definition)
D ₄ , 100% He	0.9
D ₄ , 1% O ₂	6.8
D ₄ H, 100% He	0.9
D ₄ H, 1% O ₂	4.5

5 [0027] ATR-FTIR studies of the substrate surfaces showed that ring-opening polymerisation of the D₄ and D₄H coating-forming materials had occurred to form a polysiloxane on the substrate surface. In particular, the ATR-FTIR studies on the latter showed that the polysiloxane coating retained much of the D₄H Si-H functionality.

10 [0028] NMR studies of a coating prepared as described above on a glass surface showed that the polysiloxane formed on the substrate surface by polymerisation of the D₄ and D₄H coating-forming materials comprised divalent (CH₃)₂SiO_{2/2} units and trivalent CH₃SiO_{3/2} units, i.e. the polysiloxane is resinous.

15 Example 2

[0029] The method of Example 1 above was repeated using a glass substrate and acrylic acid as the coating-forming material, and helium alone as the discharge gas. The coating was removed from the substrate prior to analysis.

[0030] FTIR and solid state NMR analysis of the coating confirmed that the acrylic acid had polymerised to form polyacrylic acid. Both FTIR and NMR data showed consumption of the unsaturated C=C bond.

25

Example 3

[0031] The method of Example 2 was repeated, but using nylon and polyethylene substrates.

- 5 [0032] An FTIR analysis comparison of the coating with commercially available polyacrylic acid confirmed that the acrylic acid coating-forming material had polymerised to form a polyacrylic acid coating on the substrate surfaces.

- 10 [0033] X-ray photoelectron spectroscopic analysis, film thickness analysis, and contact angle measurements were performed per Example 1 above. The results are shown in Table 3 below.

Table 3					
	XPS analysis			Contact	Deposition rate
	%C	%O	%CO ₂ H	Angle (°)	(nm s ⁻¹)
Theory	60.0	40.0	33.3	-	-
Commercial polyacrylic acid	63.3	36.7	29.9	wets	-
Example 3 coating	62.6	37.4	26.4	wets	231±95

- 15 [0034] Gas transport through the coated polyethylene film was determined by mass spectrometry, and the barrier improvement factor calculated per Example 1 above over an untreated polyethylene substrate and commercially available polyacrylic acid. The results are shown in Table 4 below.

Table 4	
Sample	Barrier Improvement Factor
Untreated substrate	1.0 (by definition)
Commercial polyacrylic acid	1.1±0.1
Example 3 coating	7.2±0.9

[00351] A lap shear test was performed on the coated nylon substrates as follows. Two opposing faces of coated nylon substrates were overlapped to create a joint covering 1cm², and the substrates were cured under a 2kg weight at 70°C for 60 minutes. The adhesive strength of each joint was then determined by pulling the substrates apart at a rate of 5mm per minute using a tensilometer (Instron), and recording the maximum load reached prior to failure. The coated substrates withstood a maximum load of 74±11 Ncm⁻² prior to failure. Comparison joints made from uncoated nylon displayed no adhesive properties.

Example 4

[00361] The method of Example 2 was repeated, using a glass substrate and 1H,1H,2H-perfluoro-1-octene (CF₃(CF₂)₅CH=CH₂) as the coating-forming material.

[00371] X-ray photoelectron spectroscopic analysis, FTIR analysis and contact angle measurements (with water and decane) were performed per Example 1 above, and results are shown in Table 5 below. The XPS and FTIR analysis showed that the glass substrate coating was rich in CF₂ and CF₃ and the contact angles for water and decane were determined as per example 1.

Table 5					
	XPS analysis			Contact Angle (water) (°)	Contact Angle (decane) (°)
	%C	%F	%O		
Theory	38.1	61.9	-	-	-
Example 4 coating	38.0	60.0	2.1	118.9±3.0	61.1±2.2

[0038] The contact angle measurement results show that the glass substrate has been rendered substantially hydrophobic and oleophobic by the coating.

CLAIMS

1. A method for forming a coating on a substrate, which method comprises introducing an atomised liquid and/or solid coating-forming material into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom, and exposing the substrate to the atomised coating-forming material.
2. A method according to Claim 1 wherein the coating-forming material is introduced by direct injection.
3. A method according to Claim 1 or 2 wherein the coating-forming material is a silicon-containing material.
4. A method according to Claim 3 wherein the coating-forming material is selected from a dimethylsiloxane, and a siloxane having silicon-hydrogen bonds.
5. A method according to any preceding Claim wherein the plasma is generated in an oxygen containing atmosphere.
6. A method according to Claim 1 or 2 wherein the coating-forming material is an organic or organometallic material.
7. A method according to Claim 6 wherein the coating-forming material is selected from acrylic acid and a perfluoroalkene.

- 18 -

8. A method according to any preceding Claim wherein the substrate comprises metal, ceramic, plastics, woven or non-woven fibres, natural fibres, synthetic fibres, cellulosic material, and powder.
9. A method according to any preceding Claim wherein the coating increases the adhesive, release, gas barrier, moisture barrier, electrical and thermal conductivity, optical, dielectric, hydrophilic, hydrophobic, and/or oleophobic properties of the substrate.
10. A method of producing a substrate having a multi-layered coating according to any preceding claim whereby the coating is applied by repeatedly passing said substrate through the atmospheric plasma glow discharge or by passing said substrate through a series of atmospheric glow discharge chambers.
11. A method for polymerising a polymer forming material, which method comprises atomising the polymer-forming material, and exposing the atomised polymer-forming material to an atmospheric pressure plasma discharge.
12. A method according to any one of claims 1 to 4, 6 or 7 wherein the chemical properties of the atomised liquid and/or solid coating forming material are substantially retained in the resulting coating formed.
13. A method in accordance with any preceding claim wherein the substrate is coated continuously by use of a reel to reel apparatus.

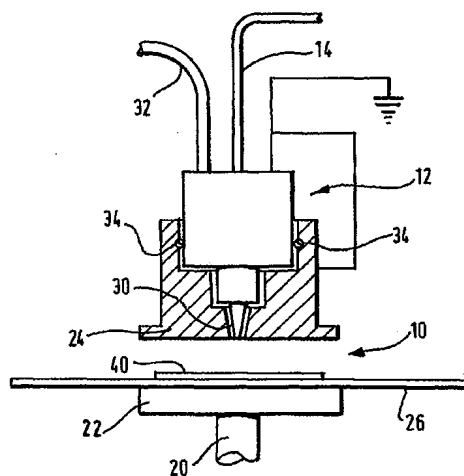
- 19 -

14. A method in accordance with any preceding claim wherein the substrate is pre-treated by exposure to plasma prior to the introduction of coating forming material.
15. A method in accordance with any preceding claim wherein the coating formed on the substrate is post-treated by exposure to plasma.
16. A method in accordance with claim 14 or 15 wherein the plasma is applied by way of atmospheric pressure glow discharge.
17. A method in accordance with claim 16 wherein an oxygen containing material is added to the plasma.
18. A method in accordance with claim 17 wherein the oxygen containing materials are selected from the group of oxygen gas and water.
19. Apparatus for forming a coating on a substrate, which apparatus comprises means for generating an atmospheric pressure plasma glow discharge within which, in use, the substrate is placed, an atomiser for providing an atomised coating-forming material within the plasma discharge, and means for supplying a coating forming material to the atomiser.
20. Apparatus in accordance with claim 19 wherein the atomiser is an ultrasonic nozzle.

- 20 -

21. Apparatus in accordance with claim 19 or 20 wherein the substrate is fixed to a reel to reel apparatus to enable a continuous coating of the substrate.
22. A coated substrate prepared in accordance with the method of any one of claims 1 to 18.
23. A coated substrate in accordance with claim 22 wherein the chemical properties of the atomised liquid and/or solid coating forming material are retained in the resulting coating.
24. Use of a coated substrate formed in accordance with the method of any one of claims 1 to 18 as a lamination adhesive, an oxygen and/or moisture barrier or in organic light emitting diode devices.

FIG. 1



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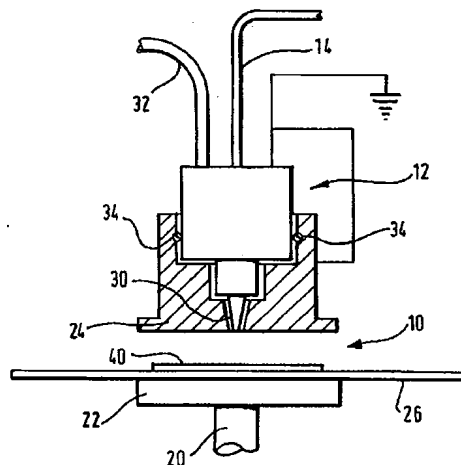
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[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR FORMING A COATING



(57) Abstract: A method for forming a coating on a substrate using an atmospheric pressure plasma discharge. The method comprises introducing an atomised liquid and/or solid coating-forming material into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom, and exposing the substrate to the atomised coating-forming material. The application also describes a method for polymerising a polymer forming material, and further to apparatus for forming a coating on a substrate.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document (as published on or after the international filing date) "L" document which may show double or priority claims or which is cited to establish the publication date of another document or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
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